ON

CITRACONIC, ITACONIC AND MESACONIC ACIDS.

INAUGURAL-DISSERTATION

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The following investigations were made in the Chemical-Laboratory of the Emperor William University in Strassburg under the direction of Professor Fittig and I would take this opportunity of most sincerely thanking Professor Fittig for the kindness he has always shown me in my work and in many other ways.

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INTRODUCTION.

The three isomeric bodies, citraconic, itaconic and mesaconic acid have been the subject of investigation for more than half a century. It was in 1822 that Lassaigne[1]) made known his discovery that by the dry distillation of citricacid a new acid was produced. His description of the attendant phenomena is essentially that of later observers. The formation of two liquids, the one watery and thin, the other oily and heavy, and slowly soluble in water when the two were mixed. From such a solution crystals of the new „Acide pyrocitrique" (citraconic acid) were obtained. Several salts were made, and an elementary analysis. Eleven years later Dumas[2]) touched upon this subject, his work being chiefly careful analyses of the lead salt of the new acid, and the identification of acetone as a by-product in its production. A great advance was made when Bauhr[3]) found that instead of one, two acids were produced, which were called „citribique" (citraconic) and „citracique" (itaconic). The fact was fully recognized that these two bodies were isomeric. Roliquet's[4]) work is only interesting from the fact that citraconic acid anhydride was shown to exist, though the nature of anhydrides was not known at this time. It was left for Crasso[5])

[1]) Ann. de Chim. et de Phys. 21. 100.
[2]) Annalen 8. 17.
[3]) Ann. 19. 29.
[4]) Ann. 25. 138.
[5]) Ann. 34. 53.

to explain clearly the production of citraconic from citric acid. He showed that aconitic acid was the direct product, and that from this the itaconic acid was formed, and citraconic acid from that. This opinion was confirmed by Swartz[1]) some years later, and when Anschütz[2]) isolated itaconic acid anhydride and proved that it was this which at a higher temperature gave the citraconic acid anhydride, each step in the process was known. That Xeronic-acid, a member of another group was also produced in small quantities as a by-product was shown by Fittig[3]).

The third isomere-mesaconic acid was first described by Gottlieb[4]), who obtained it by heating citraconic acid with dilute nitric acid. The mesaconic acid salts were investigated by Pebal[5]).

The various questions concerning these three isomeric bodies have furnished material for an almost endless number of investigations. Of great value are Kekulé's[6]) discovery and investigation of the dibromineaddition products of these bodies, and the reduction of these three to one and the same methyl succinic acid.

Of equal interest were the researches of Fittig[7]) and his pupils on the monobromineaddition products, and the decomposition products of these and the dibromineproducts when boiled with sodium carbonate solution or with water alone. Halogen hydrideaddition products were also made and investigated by Swartz[8]).

The amid, anilid, and similar compounds of these acids have been the subject of exhaustive investigation at the hands

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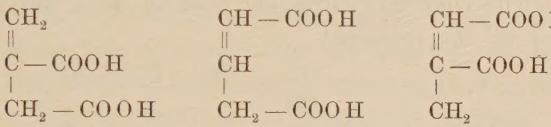
[1]) Bull. Soc. Roy. de Belgique (2) 36. Nr. 7 1873. p. 64.
[2]) Berichte 1880, 1541.
[3]) Ann. 188. 64.
[4]) Ann 77. 265.
[5]) Ann. 78. 129.
[6]) Ann. Sup. I, 338, II, 94.
[7]) Landolt, Ann. 188. 71. Krusemark, Ann. 206. 1.
[8]) Bull. Soc. Roy de Belgique (2) XVIII Nr. 11. p. 324.

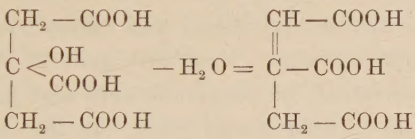
of Strecker[1]), Michael[2]), Anschütz[3]), and others[4]), and it is from conclusions drawn from this line of work that Anschütz concludes that citraconic acid is a dioxylactone.

Naturally the constitution of citraconic, itaconic and mesaconic acid has always been an interesting question, presenting as it does many difficulties, and it is a matter which today can not be considered settled. One of the earliest explanations is Henry's[5]). He proposes these three formulae:



Ita Mesa Citra

and there is much to be said in their favor, citric acid losing one molecule of water would give only one compound aconitic acid, as it is manifestly immaterial which CH_2 loses an H to unite with the OH to form water:



Aconitic acid, however could lose CO_2 in each of the three positions, giving the formulae mentioned above. The formula for itaconic acid is the generally accepted one, and many authorities have assigned his citra formula to mesa. Various other explanations of the isomerism of citraconic and mesaconic acid have been proposed. Fittig[6]) considered that this was the same as that between fumaric and maleïc acid, which opinion Bischoff[7]) confirms. The isomerism is explained

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[1]) Berichte 1882, 1639.

[2]) Berichte 1886, 1375.

[3]) Jahresberichte 1887. 1694. Berichte 1887, 3214. Berichte 1888, 3252. Annalen 254. 130.

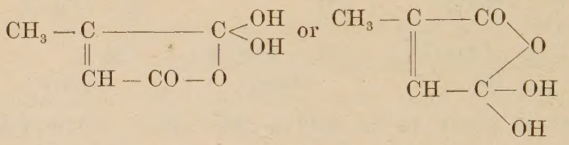
[4]) Berichte 1888, 1366. Berichte 1891, 314. Ann. 77. 265.

[5]) Bull. Soc. Chem. (2) 23. 347.

[6]) Ann. 188. 95.

[7]) Berichte XXIII, 1939.

by Fittig[1]) on the assumption of free affinities in the citraconic and maleïc acid. Conceptions of the arrangement of molecules in space have been resorted to by others, as a possible explanation. Wislicenus[2]) having elaborated the idea in his treatise on that subject. Markonnikoff[3]) was of the opinion that mesaconicacid was a polymere of citraconic acid, and though many facts seemed to favor this, the balance of opinion is against the idea. Still another explanation is that of Anschütz[4]), who considers citraconic acid to be a dioxylactone represented by the formula:



With the hope of explaining more thoroughly this much discussed question, Professor Fittig undertook with his pupils an investigation of the homologues of citraconic and mesaconic acid. Results[5]) already published and others soon forthcoming from this laboratory show that the general characteristics, physical and chemical, of citraconic acid and mesaconic acid, are also common to their homologues. In the course of these investigations several new and interesting reactions were observed and it was found needful to see if these were also common to the original citraconic group, and if so, to investigate them more carefully where an abundance of material was easily obtainable.

With this end in view the following research was undertaken at Professor Fittig's suggestion. Much earlier work on citraconic, itaconic and mesaconic acid, and also on citra and mesa-dibrommethylsuccinic acid was repeated, because it was

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[1]) Ann. 188. 95.

[2]) Räumliche Anordnung der Atome etc. Leipzig 1887. p. 37.

[3]) Berichte 9. 1440.

[4]) Berichte 13. 1541.

[5]) Glaser, Dissertation Strassburg 1890. Burwell, Dissertation Strassburg 1892. Schirmacher, Dissertation Strassburg 1892. Berichte XXVI, 40.

found, as is often the case with compounds long known, that properties it was desirable to make use of were either not mentioned at all, or very lightly touched upon. It was desirable also to have the dibrom acids for purposes of comparison.

This work of repetition may be briefly summed up as follows.

Citraconic Acid.

Citraconic acid may be easily obtained perfectly pure by dissolving the ordinary product in ether and adding ligroïn. On standing, the acid separates out slowly in the form of thin plates and needles, not in large crystals as from an aqueous solution. This method has the advantage of being more rapid than re-crystallization from water, in which the acid is extremely soluble. The pure acid melts at 91°, is soluble in ether, somewhat so in cold chloroform, more so by warming from 40° to 50°, and is insoluble in carbon disulphide, benzene, carbon tetrachloride and ligroïn.

The acid usually has a slight odor due probably to the presence of minute quantities of empyreumatic bodies from which it is difficult to entirely free it.

It is not volatile either on standing over sulphuric acid or in a vacuum, 1,1310 g were kept in an exsiccator over sulphuric acid for three months, and lost in weight 0,0080 g or 0,7 %. It was then placed in a vacuum and no further loss was observed.

Barium citraconate was made by neutralizing the acid with pure $Ba(OH)_2$, and was found to agree with earlier observations[1]).

Analysis

0,3305 g air dried salt lost at 100°, 0,0473 g H_2O with no further loss at 150°, and gave 0,2478 g $BaSO_4$.

Calculated for $C_5H_4O_4Ba + 2^1/_2 H_2O$	Found
44,10 % Ba	44,19 % Ba
14,51 % H_2O.	14,31 % H_2O.

[1]) H. Kämmerer, Ann. 170. 191.

This salt is almost insoluble in alcohol, and when alcohol is added to an aqueous solution, it is precipitated in the form of small pearly scales, which an analysis showed to be also $C_5H_4O_4Ba + 2^1/_2H_2O$.

Solubility of Barium Citraconate.

Barium citraconate is much more soluble in hot than in cold water. A cold saturated solution was prepared by dissolving the salt in hot water, allowing it to cool (temp. 12°), and filtering off the liquid from the crystals which then separated out, 7,9622 g solution gave 0,0203 g $BaSO_4$, equivalent to 0,0270 g $C_5H_4O_4Ba + 2^1/_2H_2O$. Therefore 1,0 is soluble in 293 g H_2O of 12°.

Itaconic Acid.

Itaconic acid may be easily purified by recrystallization from water, being easily soluble in hot water, and much less so in cold. It melts at 161°, is soluble in ether, insoluble in chloroform, carbon disulphide, benzene, carbontetrachloride, and ligroïn. The barium salt was prepared from pure acid and pure $Ba(OH)_2$. It was found to be more soluble in cold than in hot water. A solution of the salt was evaporated on the water-bath until crystallization began, then filtered and allowed to stand many days at ordinary temperature. No crystals could be obtained, but a crust slowly formed on the sides of the glass, increasing in quantity until the liquid was entirely evaporated.

When a hot solution in which crystallization has begun is allowed to remain a short time longer on the water-bath the salt separates out as a very voluminous precipitate having the appearance of cotton. This precipitate is very slowly soluble in cold water. Analysis shows it to contain one half molecule water of crystallization which is not driven off by heating to 150°. According to Crasso[1]) there is one molecule of water of crystallization, but his analysis agrees equally well with one half molecule.

[1]) Ann. 34. 66.

Analysis.

0,2411 g air dried salt lost 0,0005 g H_2O at 100° with no further loss at 150°—160°, and gave 0, 2037 g Ba SO_4.

Calculated for $C_5H_4O_4Ba + {}^1/_2 H_2O$	Found
50,00 % Ba.	49,69 % Ba.

Solubility of Barium Itaconate.

A cold saturated solution of barium itaconate, was prepared by allowing an excess of salt to dissolve as much as possible in cold water, and then filtering (temp. 20°), 5,7826 g solution gave 0,3886 g Ba SO_4 equivalent to 0,4569 g $C_5H_4O_4Ba + {}^1/_2 H_2O$. Therefore 1 g is soluble in 11,6 g H_2O of 20°.

Mesaconic Acid.

Mesaconic acid may also be easily purified by recrystallizing from a hot aqueous solution being much more soluble in hot than in cold water. Dissolved in ether, on the addition of ligroïn it falls out at once as a white powder, and perfectly pure. It melts at 202°, and is insoluble in chloroform, carbondisulphide, benzene, and carbontetrachloride. The barium salt was prepared from pure acid and $Ba(OH)_2$. As was found by Pebal[1]) this salt crystallizes readily, and contains four molecules water of crystallization. The last trace of water can not be removed by heating at 100° or 150°.

Analysis.

0,2310 g air dried salt lost at 100° 0,0441 g H_2O, and at 150° 0,0026 g more, — total loss of water equals 0,0467 g — and gave 0,1590 g Ba SO_4.

Calculated for $C_5H_4O_4Ba + 4H_2O$	Found
40,65 % Ba	40,48 % Ba
21,36 % H_2O.	20,21 % H_2O.

Solubility of Barium Mesaconate.

Barium mesaconate is much more soluble in hot than in cold water. When evaporated very slowly on the water-bath a supersaturated solution is sometimes obtained. A cold saturated solution was prepared by dissolving a quantity of the salt in hot

[1]) Ann. 78. 129.

water, allowing it to cool (temp. 15,5°) and filtering from the crystals which thus separated out. 6,0753 g solution gave 0,2460 g Ba SO_4 equivalent to 0,3558 g $C_5H_4O_4Ba + 4H_2O$. Therefore 1 g of the salt is soluble in 16 g H_2O of 15,5°.

Citradibrommethylsuccinic Acid.

Kekulé[1]) who first made this acid mentions that he had difficulty in obtaining it pure and in the form of crystals. Often crusts, or a thick syrup which would with difficulty crystallize, were obtained instead. To a solution of five parts of citraconic acid in three parts of water, he added the theoretical amount of bromine in small portions. It was readily combined, and the liquid became colorless. After standing some time the dibrom acid separated out, and was recrystallized from water, in which it is very easily soluble.

In general this method was followed, but it was found to be more advantageous to use even less water, not more than two parts to five parts of acid. The bromine should always be added where no direct or diffused sunlight can fall upon the mixture; otherwise, as will be explained later on, small quantities of mesaconic acid will be also produced. The raw product obtained should be pressed dry between filter paper, and recrystallized by dissolving it in ether, and adding a large quantity of ligroïn. At first a milkiness is produced, but on standing, well formed crystals slowly form on the sides of the glass used. If the acid was very impure an oil sometimes separates out also, which could not be crystallized. The pure acid melts at 150°, is easily soluble in ether, somewhat so in chloroform, and insoluble in carbondisulphide, benzene and ligroïn.

Analysis.

0,2054 g gave 0,2667 g AgBr equivalent to 0,1134 g Br.

Calculated for $C_5H_6O_4Br_2$	Found
55,17 % Br.	55,25 % Br.

[1]) Ann. Sup. II, 96.

Mesadibrommethylsuccinic Acid.

This acid was prepared as described by Krusemark[1]). To five parts of mesaconic acid suspended in six parts of water, the theoretical amount of bromine was added, in small portions, the whole being kept at a temperature of 60° to 65°. The bromine combines readily with the acid, and as the dibrom acid is much more soluble than mesaconic acid, all will be dissolved in the small quantity of water used. Allowed to cool, the dibrom acid soon separates out, and is also best recrystallized from ether and ligroïn, separating out after standing some time as small hard crystals. The pure acid, when heated rapidly melts at 190°—5°, heated very slowly it melts at 187°—8°, in each case with a violent evolution of gas. In appearance and properties it resembles citradibrommethylsuccinic acid very closely.

Analysis.

0,2056 g gave 0,2636 g Ag Br equivalent to 0,1121 g Br.

Calculated for $C_5H_6O_4Br_2$	Found
55,17 % Br.	54,56 % Br.

Citraconic Acid and Bromine.

Glaser[2]) found that when ethylcitraconic acid was dissolved in chloroform and the theoretical amount of bromine necessary to form the dibrom acid was added, mesaconic acid was formed instead when sunlight or diffused daylight was allowed to act upon the mixture.

An analogous change had been observed with maleïc acid[3]) which, under similar conditions, is in part changed into fumaric acid. There was reason therefore to expect a similar change of citraconic acid into mesaconic acid and this was found to be the case.

Five grams of citraconic acid were dissolved in chloroform free from water, by warming from 40° to 50°, and, after

1) Dissertation Strassburg 1880, p. 7.
2) Dissertation Strassburg 1891, p. 28.
3) Ann. 195. 59.

cooling, the theoretical amount of bromine 6,1 g was added to the mixture in small portions. No perceptible change in temperature was observed, and the liquid remained dark brown. The cylinder containing the mixture was then placed in bright light, though not in direct sunlight.

After a few moments, on the side of the cylinder toward the light, a white crust was observed to be forming, and soon the whole liquid was thick with a finely divided white powder. Only a trace of hydrobromic acid was observed. At the end of an hour this white powder was rapidly filtered off, and well washed with chloroform.

When dry it weighed 2,5—6 g. A portion of this acid was reduced with sodium amalgam, and found to be free from bromine. It melted at 202° and in appearance and properties was exactly like the mesaconic acid obtained from citraconic acid by treating it with dilute nitric acid. An elementary analysis was made.

0,2265 g acid gave 0,3815 g CO_2 and 0,0959 g H_2O.

Calculated for $C_5H_6O_4$	Found
C 46,15 %	C 45,93 %
H 4,61 %	H 4,70 %.

The liquid portion which was filtered off was still dark colored, scarcely lighter than at first. It was allowed to remain in the light several days, at the end of which time it was colorless. On opening the cylinder a small quantity of hydrobromic acid was observed. On the sides of the cylinder a few small crystals were found, but the quantity was too small for investigation and at this time the dibrom-acids had not been made for comparison. The chloroform was evaporated as far as possible by passing a current of dry air through it, and a thick yellow oily syrup remained which had a peculiar, penetrating and disagreeable odor, and attacked the eyes and mucous membrane very violently. This syrup after standing in a vacuum two months remained unchanged except that it was darker in color. It was soluble in all the ordinary solvents but no crystals could be obtained from it. Thinking that

perhaps the chloroform used was not free from alcohol and that to this was due the fact that no body could be isolated, another portion of chloroform was prepared with great care. It was shaken out repeatedly with water to free it from alcohol, dried with chloride of calcium and distilled, only that portion being retained which passed over at 62°. Using this chloroform as a solvent an experiment was made with five grams of citraconic acid as before, except that the mixture remained a little longer in the light before filtering. In addition to mesaconic acid, less oily liquid was obtained than before, and more crystals, which recrystallized from ether and ligroïn, had the appearance of mesadibrommethylsuccinic acid, and melted at 194°—7° with violent decomposition.

The same results are obtained if very finely pulverized citraconic acid is suspended in chloroform and treated with bromine in sunlight. In these experiments it was observed that the mesaconic acid was formed in a very short time, and that very little bromine was used to produce it, as the liquid was still dark brown when the mesaconic acid was filtered off. Therefore an experiment was made using very little bromine and as citraconic acid is so insoluble in chloroform, it was first dissolved in a little pure ether and diluted with chloroform, a mixture in which mesaconic acid is very insoluble.

3,5006 g citraconic acid were dissolved in such a mixture, and a few drops of a 25 % solution of bromine in chloroform added. The bottle was placed in direct sunlight, and almost immediately a precipitation on the side toward the light was observed. Soon the whole appeared solid so much mesaconic acid had been precipitated. It was at once filtered off, and washed with chloroform. The liquid was a little lighter in color than at first, so a drop or two more bromine solution was added, and it was again placed in the sunlight. A second precipitate was thus obtained which was filtered off as before and in the same way a third precipitate was also obtained, very small in quantity. No trace of hydrobromic acid was observed. These three precipitates of mesaconic acid weighed 2,2286 g, were free from bromine and melted at 202°. When

the liquid was again placed in sunlight, a little more bromine solution being added, it became slowly colorless, but no more mesaconic acid was precipitated. It was therefore evaporated as much as possible by passing a current of dry air through it, and a little white substance having the appearance of mesaconic acid, and a small quantity of oily liquid was left. All was dissolved in ether, and a quantity of ligroïn added, since the mesaconic acid, if present, would be at once precipitated, the dibrom acids, on the contrary, only after standing some time.

In this manner a very little mesaconic acid, 0,0783 g was obtained, and when the ether-ligroïn had evaporated somewhat by standing, 0,0310 g substance was obtained which melted with decomposition at 190°—5°, but the quantity was so small that it could not be said whether it was impure mesaconic or mesadibrommethylsuccinic acid.

When the ether-ligroïn had stood some time longer 0,0383 g of small hard crystals of citradibrommethylsuccinic acid, melting at 150°, were obtained.

Evaporating the liquid slowly as much as possible, a little of the bad-smelling oil mentioned before, was obtained which was placed in an exsiccator. After standing a few days it became perfectly black, like tar in appearance, and could not be investigated further. In this experiment 2 g of 25 % bromine solution were used i. e. 0,5 g bromine. The theoretical amount would have been 4,3 g.

The mixture was in the sunlight about one hour and 2,3069 g or 65,9 % of the possible amount of mesaconic acid were obtained. Mesaconic acid made by this process is always perfectly white, that obtained by treating citraconic acid with nitric acid, has usually a somewhat yellow color which can be with difficulty removed by recrystallization.

A second experiment was made as above. 3,4006 g citraconic acid gave 1,9714 g mesaconic acid, i. e. 57,9 %, also 0,0622 g melting at 194°—7°, 0,0383 g citradibrommethylsuccinic acid melting at 150°, and a little black tarry substance.

Using a smaller quantity of citraconic acid practically the same results were obtained:

1. 1,0000 g citra gave 0,6850 g mesaconic acid i. e. 68,5 %.
2. 1,0000 g „ „ 0,6590 g „ „ „ 65,9 %.

Though much better results are obtained by using a medium free from water as a solvent for the citraconic acid, it is by no means necessary to do so.

2,1497 g of citraconic acid were dissolved in a little water, a drop or two of bromine added, and placed in the sunlight. Almost immediately a precipitation of finely divided white substance was observed, first on the side toward the light. This was filtered off, washed with a little water and allowed to dry. The liquid became lighter colored much more rapidly than when chloroform was used as a solvent. A drop or two more of bromine was added, and a second precipitate obtained which was placed with the first. On adding a little more bromine the liquid became, in the light, slowly colorless without further precipitation.

0,2189 g substance were obtained, which as its appearance and melting point 202°, plainly showed, was mesaconic acid.

It will be seen that citradibrommethylsuccinic acid should always be prepared where no sunlight can affect it. Otherwise small quantities of mesaconic acid will be also produced. This was the case with a specimen prepared without this precaution.

Experiments with many homologues of citraconic acid, in part already published[1], have shown that the above is a general method of obtaining the corresponding mesaconic acids, and to be preferred to the older method with nitric acid on account of its rapidity and the large amount of acid obtained.

In the analogous case of fumaric acid obtained from maleïc by the action of bromine (and light) Wislicenus[2]) advances the theory that from the maleïc acids, isodibrom-

1) Glaser, Dissertation Strassburg 1890. Burwell, Dissertation Strassburg 1892. Schirmacher, Dissertation Strassburg 1892. Berichte 1893, 46.

2) Ann. 246. 67.

succinic acid is formed as intermediate product. This acid then splits off one molecule of hydrobromic acid which immediately unites with the unchanged maleïc acid present. The monobromsuccinic acid thus formed, at once loses a molecule of hydrobromic acid experiencing at the same time a molecular rearrangement, and fumaric acid is produced.

The cause of these changes was considered to be the heat evolved by the union of bromic and maleïc acid, and also the water used as a solvent. In the experiments with citraconic acid, water can evidently play no part, as it was excluded in every case except one. As the next experiment shows, the union of citraconic acid and bromine, in a medium, free from water, is a slow one; so the heat produced at any one time must be very slight, and in none of the experiments was there a noticeable change in temperature. Various of the possible intermediate conditions were also investigated, but in no case was mesaconic acid found.

Citraconic Acid and Bromine without Light.

3,5883 g citraconic acid were dissolved in a little ether and diluted with chloroform, 4,5 g bromine, the amount necessary to form a dibrom-acid, were added in the dark, the cylinder containing the mixture was carefully wrapped in dark paper, and placed where it could receive no light. A perfectly similar experiment, which was examined each evening by gas light, had shown that ten days to two weeks were necessary for the acid and bromine to unite, and the liquid become colorless. This portion, therefore, was allowed to remain undisturbed several weeks, and on examination it was then found that the bromine and acid had all combined. When the stopper of the cylinder was removed no hydrobromicacid was observed. The colorless liquid was evaporated with a current of dry air, as much as possible, and a thick syrup remained which, on standing a few days, under an exsiccator became nearly solid and crystalline. The unpleasant odor, before mentioned in these experiments was noticed on opening the exsiccator.

This crystalline mass was dissolved in ether, in which it was easily soluble, and a quantity of ligroïn added. A slight milkiness was produced but no precipitation of mesaconic acid. After standing a few hours crystals were observed to be forming on the sides of the vessel.

These slowly increased in size, and number. After standing a few days they were separated from the liquid, well washed in ligroïn and, when dry, weighed 4,5827 g. From the appearance and melting point 150° this was plainly citradibrommethylsuccinic acid. The ether-ligroïn was allowed to evaporate slowly over sulphuric acid and 0,7817 g more small hard crystals, also melting at 150°, were obtained.

Further evaporation yielded crystals somewhat yellow in color which were recrystallized, weighed 0,1535 g and melted at 150°. No more crystals could be obtained but when the ether ligroïn was entirely evaporated a little thick, ill-smelling liquid remained, which on standing a short time became black and like tar and with which nothing further could be done. No trace of mesaconic acid or other body than citradibrommethylsuccinic acid could be obtained. Of the latter there were 5,5179 g or 68,93 % of the theoretical amount.

Citraconic Acid, Hydrobromic Acid and Sunlight.

1,000 g citraconic acid was dissolved in a very little pure ether, diluted with chloroform and three or four drops of hydrobromic acid (saturated at 0°) were added. The mixture was exposed to sunlight five hours, but no mesaconic acid was precipitated. The solvent was evaporated as usual, and the remainder dissolved in a very little water, in which it was easily soluble, and placed in an exsiccator.

In a few days crystals were found which the melting point 91° showed to be unchanged citraconic acid.

A portion of citraconic acid which was treated in a similar way with dry hydrobromic acid gas, also gave no mesaconic acid.

Citraconic Acid and Light.

1,0017 g citraconic acid were dissolved in pure ether and chloroform, and exposed to sunlight ten hours. No mesaconic acid was precipitated and on evaporation the citraconic acid was recovered unchanged, melting at 91°.

Citradibrommethylsuccinic Acid and Light.

0,500 g citradibrommethylsuccinic acid in chloroform, was exposed to the light three days. On evaporating the chloroform the acid was recovered unchanged, melting at 150°.

Citradibrommethylsuccinic Acid, Citraconic Acid, and Light.

0,80 g of the dibrom acid and 0,40 g of citraconic acid, in chloroform, were exposed to the light several days, no mesaconic acid was precipitated, and when the chloroform was evaporated, the dry acid left was soluble in a few drops of ether or water, and so far as could be seen, was unchanged.

Citradibrommethylsuccinic Acid, Bromine, and Light.

To 1,00 g citradibrommethylsuccinic acid, in chloroform, a few drops of bromine were added. The mixture remained in sunlight nine hours, was unchanged in color, and no mesaconic acid was precipitated.

Removing the solvent as usual, the acid was recovered, unchanged, melting at 150°.

Citraconic Acid, Chlorine, and Light.

A current of dry chlorine was passed into 1,00 g citraconic acid in chloroform, in bright sunlight. No mesaconic acid was precipitated, though the mixture remained in the light several days.

Swartz[1]) found that chlorine united best with citraconic acid under the influence of sunlight, dichlorcitraconic acid being produced, though it was not isolated.

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[1]) Jahresberichte 1873, 582.

Citraconic acid and light transmitted through a bromine solution.

When a test tube containing citraconic acid in chloroform, and surrounded by a solution of bromine in chloroform, was exposed to sunlight, no mesaconic acid was produced.

These experiments, besides being evidence against a dibrom addition product as an intermediate step in the formation of mesaconic acid from citraconic acid, show conclusively that both, bromine and light are necessary factors in the change, and the bromine must be in direct contact with the citraconic acid.

Citraconic Acid Anhydride and Bromine.

When citraconic acid anhydride is heated with bromine in sealed tubes, bromcitraconic anhydride is produced, together with large quantities of hydrobromic acid. This anhydride has the formula $C_3H_3Br(CO)_2O$, melts at 99° to 100°, crystallizes readily in large plates, and is easily soluble in boiling carbon disulphide[1]).

5,0883 g pure citraconic acid anhydride (colorless, and distilling at 214°), was dissolved in chloroform, in a glass cylinder having a chloride of calcium tube passing through the stopper which was also of glass. 8,3 g bromine, the theoretical amount necessary to form a dibrom addition product, were added, and the whole exposed to the sunlight. For several days no change in color was observed, but on long standing it became lighter, and at the end of two months was entirely colorless, and small crystals were formed on the sides of the glass. On opening the bottle no hydrobromic acid was observed.

The chloroform was evaporated as usual with a current of dry air, leaving a thick yellowish liquid which was placed in a vacuum over sulphuric acid. An attempt was made to purify the crystals by recrystallization from ether and ligroïn but by mistake some ether was used which was not free from water. Crystals, yellowish in color and a little brownish liquid,

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1) Krusemark, Dissertation p. 26. Strassburg 1880.

having the disagreeable odor often mentioned, were obtained. These crystals, though impure, were evidently citradibrommethylsuccinic acid, as the melting point 149°—150° and a bromine estimation agreed very nearly with that body.

0,2103 g gave 0,2693 g Ag Br equivalent to 0,1146 g Br.

Calculated for $C_5H_6O_4Br_2$	Found
55,17 % Br.	54,49 % Br.

The liquid portion which was placed in a vacuum, after standing a few days became solid and crystalline. It was pressed dry between filter paper and a bromine estimation made. The amount of bromine found, agrees quite nearly with that calculated for citradibrommethylsuccinic acid anhydride.

0,2019 g gave 0,2757 g Ag Br equivalent to 0,1173 g Br.

Calculated for $C_5H_4Br_2O_3$	Found
58,82 % Br.	58,11 % Br.

This body is not easily soluble in cold water, it first forms an oil which falls to the bottom, and slowly dissolves. It is somewhat soluble in carbondisulphide and ligroïn by warming, less so in chloroform, but from neither could good crystals be obtained.

It melts at 85°—90°, heated above its melting point, in a paraffine bath, it decomposed, giving off gas, and at about 150° vapors which were apparently bromine.

Unfortunately the quantity of substance obtained was not sufficient for further investigation.

Many years ago it was observed that when a concentrated aqueous solution of citraconic acid was heated for some time in sealed tubes, from 100° to 170° (but at 150°), it was largely converted into itaconic acid, further, from a similar solution of citraconic or itaconic acid heated from 180° to 200°, mesaconic acid was obtained [1]).

[1]) Bull. Acad. Royale de Belgique (2) 36, Nr. 7.

Evidently in near relation to this is the fact that when certain unsaturated acids are boiled with a strong sodium hydroxide solution, a change in the position of the double bond is also produced. A fact which was pointed out by Buri[1]) and others[2]). Later investigations[3]) have shown that with monobasic acids this change of position takes place in a direction toward the carboxyl group.

Citraconic Acid and Water at 100°.

According to Robiquet[4]) and Gottlieb[5]) when citraconic acid is heated for some time with water at 100°, it is in part changed into itaconic acid. Each of these observers used small quantities of acid, and the results seemed somewhat uncertain. Therefore the two following experiments were made, and their opinion was not confirmed.

2,50 g citraconic acid were dissolved in 50 ccm water, and boiled twenty-four hours in a small flask connected with a reversed condenser, a very small flame being used to avoid any danger of over-heating. The solution was then repeatedly evaporated with water, over a water-bath, since citraconic acid, or rather its anhydride which is produced at this temperature, is volatile with steam[6]), and can thus be separated from itaconic or mesaconic acid. In this case a very little brownish substance remained, not at all like itaconic acid, since it was soluble in a drop or two of water and would not crystallize. A second portion of citraconic acid, 5,00 g was dissolved in a little water and distilled with steam many days, or until an acid-distillate was no longer obtained. The small quantity of liquid remaining in the distilling-flask was still slightly acid, and was neutralized with a drop or two of bariumhydroxide solution, and evaporated to very small volume on the water-

1) Annalen 216. 171.
2) Weinstein, Ann. 227. 31. Regel, Berichte XX, 414.
3) Berichte XXIV, 82.
4) Ann. 25. 138.
5) Ann. 77. 265.
6) Ann. 188. 66.

bath. No barium itaconate was precipitated, but on the addition of alcohol a very little salt having the appearance of barium citraconate was obtained, the quantity was however too small to investigate further.

The changes which various of the homologues of citraconic, itaconic and mesaconic acid undergo on boiling with strong sodium hydroxide solution have been investigated in this laboratory, and the results in part published together with a note on the yet unpublished. Jortron[1]), Burwell[2]) found that isopropylitaconic acid remained unchanged while isopropylcitraconic acid was converted largely, and isopropylmesaconic acid in lesser quantity into isopropylitaconic acid.

From neither isopropylitaconic or mesaconic was the citraconic acid formed.

Similar results were obtained by Schirmacher[3]) with isobutylitaconic, citraconic and mesaconic acid. Citraconic, itaconic and mesaconic acid agree with the last two groups in so far that from neither, itaconic or mesaconic is citraconic acid produced, and differ in the fact that here mesaconic is the more stable form.

While the following experiments were in progress Delisle published the results of his investigations with strong sodium hydroxide and citraconic and mesaconic acids[4]). As these did not agree with the results obtained here, in several particulars the work already done was most carefully repeated, and the results first obtained were confirmed. Briefly Delisle's work was as follows. Experiments were made on the influence of variations in the strength of the sodium hydroxide solution, in the time of boiling, and in temperature. Itaconic acid was not investigated, and he concludes that while citraconic acid is largely converted into mesaconic, small quantities of itaconic- and unchanged citraconic acid are also always present. Mesaconic acid while remaining largely unchanged yields also

1) Berichte XXVI, 48.
2) Dissertation Strassburg 1892, p. 36.
3) Dissertation Strassburg 1892, p. 23.
4) Berichte 1891, 3620. Ann. 269. 74.

small quantities of itaconic and citraconic acid. The citraconic acid was identified by means of a calcium salt. While a doubt might arise by this method, such is not the case with the method here employed, which differs also in several other particulars.

Itaconic Acid and Sodium Hydroxide.

I. 5,0000 g of itaconic acid were dissolved in a 10 % sodium hydroxyde solution containing ten times the amount of alkali necessary for neutralizing the acid (NaOH 40 g, H_2O 324 g). This was boiled six hours in a copper-flask connected with a reversed condenser. When cold, the mixture was well acidulated with sulphuric acid, and extracted by shaking out with ether. This was done between seventy and eighty times, though most of the product which weighed 4,4 g was obtained in the first six extractions. The quantity of liquid which was extracted was necessarily large, but when it was made slightly alkaline with sodiumcarbonate, evaporated to small volume, acidulated and again extracted with ether, no more organic substance could be obtained.

This loss of about 0,5 g was found in all the experiments made, and may perhaps be due to the formation of an oxy-acid which could not be extracted with ether, at least repeated experiment has shown that the loss was a constant factor, and could not be avoided.

The 4,4 g raw product obtained by extraction was a nearly white, solid mass. It was dissolved in hot water, and on cooling a quantity of substance was precipitated in the form of a warty crust, which was separated from the liquid, and weighed, when dry, 2,3618 g. Its appearance, solubility and melting point 202° showed it to be mesaconic acid. The liquid filtered off from this precipitate, was placed in a small flask and distilled with steam in order to separate citraconic acid, if any had been formed.

A neutral distillate was obtained, nevertheless, as small quantities of citraconic acid, if present, might be scarcely

noticeable. The distillation was continued for ten hours. The distillate was made slightly alkaline with sodium carbonate, evaporated to very small volume, acidulated and extracted many times with ether, but nothing was obtained, so citraconic acid was not present. The contents of the distilling-flask evaporated to small volume, on cooling precipitated 0,7982 g mesaconic acid (m. p. 202°), and on further evaporation 0,2384 g more (m. p. 202°) were obtained. Evaporating the liquid still further, besides mesaconic acid crystals of a different substance were observed. These had the appearance of itaconic acid, and were found to melt at 161°. Delisle had separated small quantities of itaconic and mesaconic acid by means of a calcium salt. On trial the barium salt seemed better suited to this purpose since barium mesaconate crystallizes easily, but the best as well as the simplest method was found to be repeated crystallization from small quantities of water when the two acids could be separated mechanically. In this way 0,1432 g more mesaconic acid were obtained making a total of 3,5614 g, and 0,7155 g itaconic acid. The itaconic acid therefore had been largely changed into mesaconic acid, no citraconic acid being produced.

In all the following experiments exactly the same method was pursued, the only varying factor being the time of boiling with the sodium hydroxide solution.

II. 5,0000 g itaconic acid boiled as before, twenty-four hours yielded 3,4421 g mesaconic acid, and 1,1617 g itaconic acid, and again no citraconic acid was found.

Mesaconic Acid and Sodium Hydroxide.

I. 5,0000 g mesaconic acid boiled six hours with 10 % sodium hydroxide solution on acidulating and extracting yielded 3,5982 g mesaconic acid, and 0,8310 g itaconic acid, but no citraconic acid.

II. 5,0000 g mesaconic acid boiled with sodium hydroxide solution twelve hours yielded 3,3307 g mesaconic acid, 0,9512 g itaconic acid and also no citraconic acid. It is seen that mesa-

conic acid follows the rule of its higher homologues, being partly changed into itaconic acid. Since itaconic acid is largely converted into mesaconic acid by the same process, it forms an exception to the general rule. A state of equilibrium is reached between the two acids.

Citraconic Acid and Sodium Hydroxide.

5,0000 g citraconic acid were boiled with the sodium-hydroxide solution twenty-four hours. Extracting and separating as before no citraconic acid was found but 3,1391 g mesaconic and 1,1391 g itaconic acid were obtained.

Since here also mesaconic acid was the chief product, it was of interest to see if it was formed directly from the citraconic acid or if itaconic acid was the intermediate product. Therefore 5,0000 g citraconic acid were boiled one hour with sodium hydroxide solution. On acidulating and extracting 4,4958 g substance were recovered. This was distilled with steam and the distillation continued for some time after the distillate had ceased to be acid, that all the citraconic acid might be separated. The contents of the distilling-flask, which was not volatile yielded 0,5502 g mesaconic acid and 0,9214 g itaconic acid. Since the short action of the alkali produces twice as much itaconic as mesaconic acid, it is extremely probable that itaconic acid is the direct product, and that it is this and not the citraconic acid which is converted into mesaconic acid.

It is interesting to note, in this connection, that before the action of strong alkali on unsaturated acids was understood, the fact had been observed, though not attributed to this cause. Barbiglia[1]) attempted, without success, a synthesis of tricarballylic acid using itaconic acid, and hydrocyanic acid as a starting point. He obtained a thick liquid which he distilled. The distillate must have been largely citraconic acid anhydride, since it passed over at 200° to 215°,

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[1]) Jahresberichte 1874, 608.

and from a portion of it crystals of citraconic acid were obtained. A second portion heated in sealed tubes with dilute H_2SO_4 yielded itaconic acid. A third portion was boiled for a long time with potassium hydroxide, and quantities of mesaconic acid were obtained.

The Effect of higher Temperature on Citraconic Acid Anhydride.

During an investigation of phenylitaconic acid, the results of which will soon be published by Mr. Brooke, it was found that phenylcitraconic acid anhydride, when heated above its melting point, at 130° to 160° was converted almost entirely into phenylitaconic acid anhydride. This property, if common to all citraconic acid anhydrides, might explain the fact that citraconic acid is converted into itaconic acid when heated in sealed tubes from 130° to 160°.

The following experiments show that ordinary citraconic acid anhydride is not converted into itaconic acid anhydride at this temperature, so in the case of phenylitaconic anhydride the change is probably due to the influence of the phenyl group.

1,315 g pure citraconic anhydride were heated in a sealed tube, in a paraffine bath, one hour at 120°; no change in appearance being observed, it was further heated at 130° for four hours, when it became slightly colored. The tube was allowed to cool and placed in a freezing mixture, that the itaconic acid anhydride, if present, might crystallize. No crystals were obtained, and the liquid in the tube was dissolved in water in which it was easily soluble by warming, and repeatedly evaporated, on a water-bath, with small quantities of water, until only a very little tarry matter remained.

If itaconic acid had been present, it must have been found, since it is not volatile with water-vapor. A second portion of 3,437 g pure anhydride was heated in the same way as the first, for four hours at 155° to 160°. It became quite brown and on opening the tube a little gas was found to have been formed, and a little larger quantity of tarry

matter remained after evaporating with water-vapor. Otherwise exactly the same results were obtained as in the first case.

The Reduction of Itaconic Acid.

The reduction[1]) of isopropyl and isobutylitaconic acid with sodium amalgam can be effected with difficulty, and only in a solution which is kept constantly acid.

Kekulé[2]) however experienced no difficulty in the reduction of itaconic acid and the idea suggested itself that here also the sodium hydroxide formed by the process exercised an influence, and that in reality mesaconic was the acid reduced.

Two portions of itaconic acid were therefore reduced, the one in a warm alkaline solution, and the other in a solution which was kept cold, and slightly acid. In each case the same methylsuccinic acid was produced.

Reduction in Alkaline Solution.

6,73 g itaconic acid were dissolved in water and placed on a water-bath, 5,75 g sodium amalgam (4 %) were slowly added in small portions. When the evolution of hydrogen had ceased, the strongly alkaline solution was separated from the mercury and distilled for a short time. A neutral colorless distillate was obtained, as was also the case, when the solution was acidulated with sulphuric acid and again distilled. A volatile strong-smelling body is not produced here as in the reduction of certain of the itaconic acid homologues[3]).

The strongly acid solution was extracted with ether and a thick liquid obtained which soon became solid and crystalline.

Recrystallizing from water in which the acid was easily soluble crystals were obtained, which the melting point 112° showed to be methylsuccinic acid.

6,04 g were obtained, 89 % of the theoretical amount.

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[1]) Burwell, Dissertation Strassburg 1892. Schirmacher, Dissertation Strassburg 1892.

[2]) Ann. Sup. I, 343.

[3]) Burwell and Schirmacher dissertations.

Reduction in Acid Solution.

5,00 g itaconic acid were dissolved in water, and 250 g 4 % sodium amalgam added in small portions. The liquid was kept acid by adding dilute sulphuric acid from time to time, and was also kept cold by placing the vessel containing it in cold water. In this also there was no trace of a volatile compound produced. The strongly acidulated liquid was extracted with ether, and again a thick liquid which soon became crystalline was obtained. It was found on recrystallizing and making a melting point, that this was not a single substance; it melted only partially at 112°, a portion melting slowly some degrees higher.

It being probable that the impurity was unreduced itaconic acid, the whole was dissolved in water, and a further reduction effected as at first, 200 g more sodium amalgam being used. Again extracting with ether and recrystallizing from water 4,72 g or 94 % of the theoretical amount of methylsuccinic acid were obtained, melting at 112°.

Itaconic acid is, in reality, much more easily reduced than its homologues, and the reduction is not due to the production of mesaconic acid first.

Conclusion.

In brief the results of this research are:

1. Citraconic acid is largely converted into mesaconic acid, under the influence of bromine and sunlight, the change being apparently direct, and without the formation of citradibrommethylsuccinic acid as an intermediate product.

2. In sunlight, bromine unites slowly with citraconic acid anhydride, and forms citradibrommethylsuccinic acid anhydride.

3. Citraconic acid is not converted into itaconic acid by heating with water at 100°. Citraconic, itaconic or mesaconic acid, boiled a sufficient time with sodium hydroxide solution yields a mixture of itaconic and mesaconic acid, the latter being largely in excess over the former. In the case of

citraconic acid, itaconic acid is formed as an intermediate product, and the mesaconic acid from this.

4. Citraconic acid anhydride is not converted into itaconic acid anhydride by heating at a higher temperature.

5. Itaconic acid is reduced with comparative ease either in acid or alkaline solution, yielding in each case the same methylsuccinic acid with nearly quantitative results.

LEBENSLAUF.

Ich, Charles Ford Langworthy, wurde geboren am 9. August 1864 zu Middlebury, Kreis Addison im Staate Vermont der vereinigten Staaten von Nordamerika. Von 1870 an besuchte ich die Public Schools in Middlebury, die ich 1883 absolviert hatte; dann trat ich in das Middlebury College ein, das ich 1887 mit dem Grade eines „Bachelor of Arts“ verliess. 1890 verlieh mir dieses Institut den Titel eines „Master of Arts“.

Von 1887 an widmete ich mich zwei Jahre privaten Studien. 1889 kam ich nach Deutschland und wurde an der Universität Strassburg immatriculiert, der ich bis jetzt angehört habe.

Meine Lehrer daselbst waren die Herren Professoren Fittig, Rose, Kohlrausch, Graf zu Solms-Laubach, Zacharias und die Herren Privatdocenten Wolff, Marburg, Wortmann.

Allen diesen Herren spreche ich für die Unterstützung, welche mir dieselben bei meinen Studien gewährt haben, meinen innigsten Dank aus.